Analysis of the specific heat and calculation of the entropy, enthalpy, and free energy close to the lower phase transition in imidazolium perchlorate

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1. Introduction

Organic-inorganic molecular ferroelectrics have potential applications in science, technology, and industry. Imidazolium salts (IMSs), for example, can form hydrogen bonds with proteins and drugs [1]. IMSs have unusual catalytic properties [2,3] and wide chemical stability [4] that lead these materials to be used as electrolytes. Organic-inorganic molecular ferroelectrics come into prominence compared to ferroelectric oxides due to their advantageous properties (such as being environmentally friendly, low cost, and mechanically flexible structure) [5,6]. Imidazolium perchlorate ($C_3N_2H_5ClO_4$ or Im-ClO₄), which is the subject material of the present study, is a member of organic-inorganic molecular ferroelectrics. Im-ClO₄ exhibits superior electromechanical coupling that surpasses that of PZT films, as reported earlier [7]. Im-ClO₄ become an attractive lead-free alternative since electromechanical coupling is important for a variety of applications in electro-optics and sensor technology. Moreover, Im-ClO₄ has been reported [8] to be used as an effective 3D printed metamaterial that produces rapid-prototype for reducing the manufacturing item of ferroelectrics from hours to minutes.

Pajak *et. al.* [9] have carried out the proton NMR relaxation, the differential scanning calorimetry (DSC), and the second-moment measurements to investigate the appearance of the ferroelectricity, molecular dynamics, the polymorphic phase transitions, and the molecular structure of Im-ClO₄. Three successive solid-solid phase transitions at 487, 373, and 247 K, respectively, have been reported in their study for Im-ClO₄. They also pointed out that, the crystal structure of Im-ClO₄ is trigonal with a space group R3m, Z=1, and the lattice parameter *a* = 5.484(1) Å with α = 95.18(2)º at room temperature. Also, they stated that perchlorate ions are ordered while cations are strongly disordered at room temperature. Although all ionic sublattices are disordered, the crystal structure is also trigonal above the room temperature, with a space group R3m, a = 5.554(1) Å and α = 95.30(2)º [9]. The birefringence, dielectric, and x-ray diffraction measurements of Im-ClO₄ have been performed by Czapla *et al.* [10] to explore the dielectric and optical properties of this material. Przeslawski and Czapla have declared

[11] precise ac calorimeter measurements of the specific heat changes of Im-ClO$_4$. Very recently, we have calculated the relaxation time and the activation energy of this crystal close to the lowest phase transition temperature of 247 K [12].

In the present study, the abnormal behavior of the observed [11] specific heat data was analyzed in terms of the Ising model close to the lowest solid-solid phase transition temperature of 247 K in Im-ClO$_4$. We deduced the critical exponent values from the specific heat data [11] also, we interpreted the nature of the phase transition based on the theoretical models. In addition, the extracted values of the critical exponents were then used to predict the entropy, the enthalpy and the Gibbs free energy of Im-ClO$_4$ in the vicinity of the lowest phase transition temperature of 247 K. The Isıng model have been used in our earlier studies [13-17] to investigate the phase transition mechanism of some ferroelectric materials.

Below, "Calculation and results" was given in section 2. The "Discussion" and "Conclusions" parts were given in sections 3 and 4, respectively.

2. Calculations and Results

An Ising model can be used to calculate the free energy due to the nearest neighbor interactions $F_I(J(V), T)$ according to

$$F_I(J(V), T) = -kT\phi(J(V), T) \tag{1}$$

where J(V) is the interaction parameter, $\phi(J(V), T)$ is the natural logarithm of the partition function $Z = \sum_{ij} e^{-\frac{H_I}{kT}}$. The Ising Hamiltonian H_I can be defined in terms of the Ising spin variables σ_i and σ_j which reads as

$$H_I = -J(V) \sum_{i,j} \sigma_i \sigma_j \tag{2}$$

A power-law formula has been considered [18] to describe the critical behavior of F_I close to the phase transitions given by

$$F_I = J[A_0 + A|\varepsilon|^{2-\alpha}] \tag{3}$$

where A_0, A are constants, $\varepsilon = \frac{|T-T_C|}{T_C}$ is the reduced temperature and α is the critical exponent. From Eqs. (1) and (3) one finds

$$\phi(J(V), T) = -\frac{J}{kT} [A_0 + A|\varepsilon|^{2-\alpha}] \tag{4}$$

The second derivative of ϕ, $(\ddot{\phi})$ with respect to its argument J/kT is

$$\ddot{\phi} = -\frac{kT^2}{JT_C}(2-\alpha)\left[(A-1)|\varepsilon|^{1-\alpha} + \frac{AT}{T_C}(1-\alpha)|\varepsilon|^{-\alpha}\right] \tag{5}$$

An approximated analytical expression for the specific heat at constant volume $C_{VI} = k(\frac{J}{kT})^2 \ddot{\phi}$, has been derived [19] by neglecting the weakly divergent $|\varepsilon|^{1-\alpha}$ term in Eq.(5) which reads as;

$$C_{VI} = -\frac{JAT}{T_C^2}(1-\alpha)(2-\alpha)|\varepsilon|^{-\alpha} \tag{6}$$

The anomalous behavior of the measured [11] specific heat data was analyzed according to Eq (6) close to the phase transition temperature of Im-ClO$_4$. Interestingly, two peaks at T=245.8 K and 247.1 K have been obsd [11] for the specific heat. For this reason, 245.8 K and 247.1 K have been considered as the transition temperatures. The analysis (Eq. 6) has been carried out below and above of these two temperatures. Figure 1 shows $ln(Cp/T)$ versus $ln(\varepsilon)$ in the vicinity of these transition temperatures (245.8 K and 247.1 K). The interaction parameter

JA and the critical exponent α deduced from Fig (1) were given in Table 1 within the temperature intervals indicated.
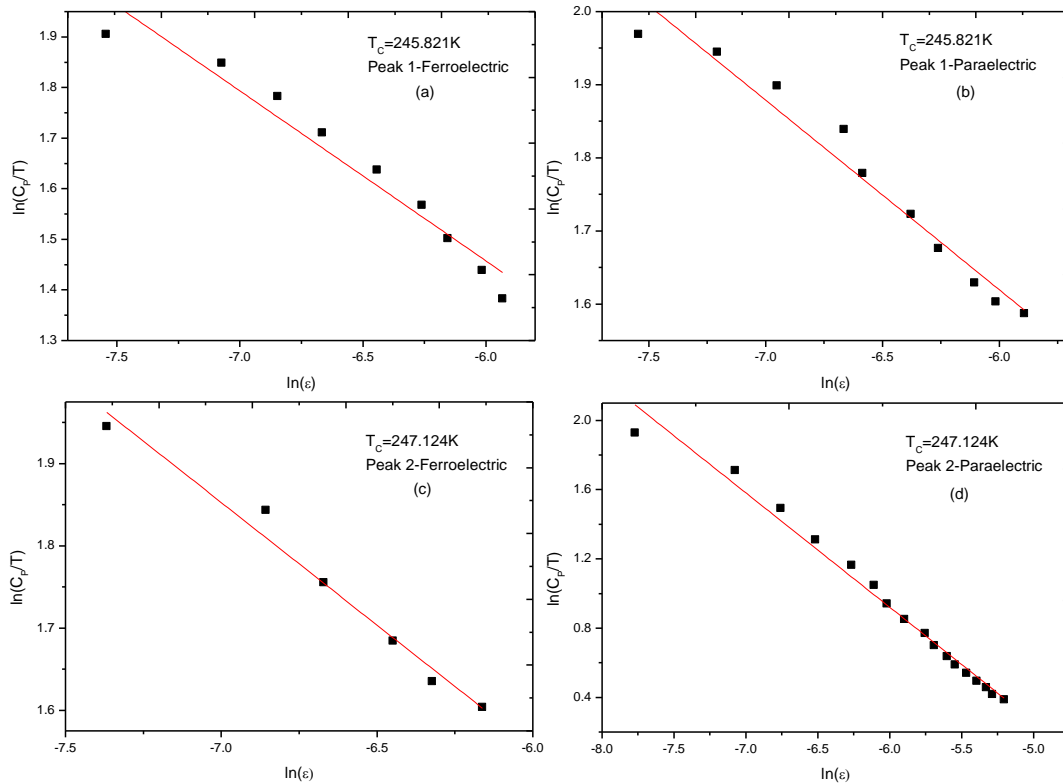

Figure 1. Specific heat C_p as a function of reduced temperature ϵ in an ln-ln scale according to Eq. (6) for the first peak at T_{C1}= 245.8 K below (a) and above (b) T_C, and the second peak at T_{C2}=247.1 K below (c) and above (d) T_C in Im-ClO$_4$. The solid lines are guide to the eye.

On the other hand, the thermodynamic definition of the enthalpy $H = \int C_P \, dT$ can be used to predict the temperature dependence of H close to the phase transition temperature T_C. Assuming that C_P has the same form of Eq. (6), after some steps, the enthalpy (H) can be obtained as

$$\Delta H = H - H_0 = -JA[(1-\alpha)|\varepsilon|^{2-\alpha} + (2-\alpha)|\varepsilon|^{1-\alpha}] \tag{7}$$

where H_0 is the enthalpy value at $T = T_C$.

Similarly, from the definition of entropy $S = \int (C_P/T) \, dT + S_0$, one can calculate the entropy as a function of temperature by replacing Eq. (6) in this basic definition which gives

$$\Delta S = S - S_0 = -JA\frac{(2-\alpha)}{T_C} |\varepsilon|^{1-\alpha} \tag{8}$$

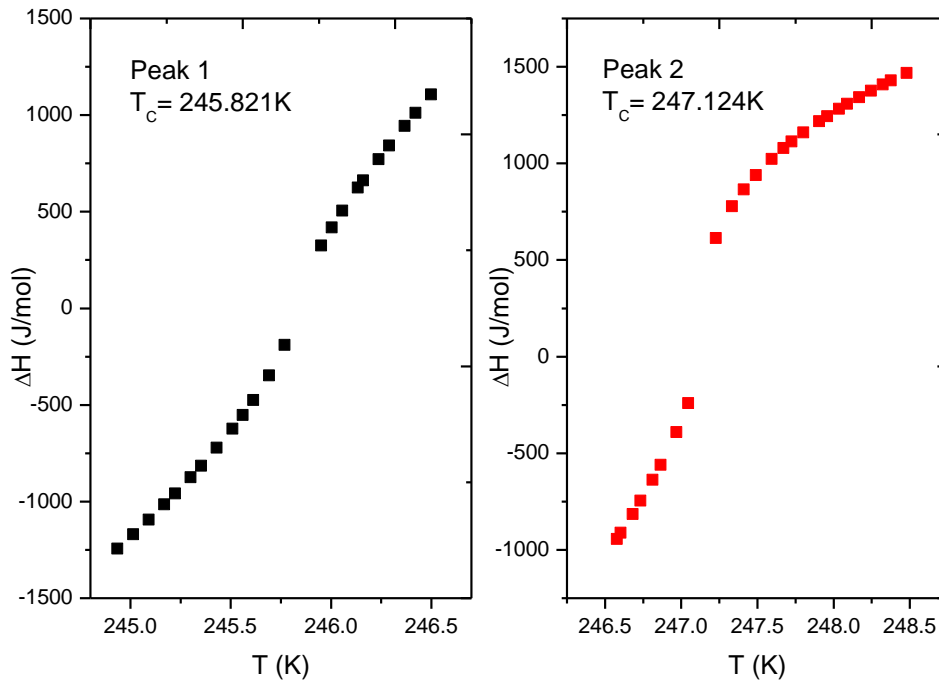where *S₀* is the entropy at the transition temperature.

Figure 2. The enthalpy difference ΔH as a function of temperature according to Eq. (7) close to the phase transition temperatures of T_{C1}= 245.8 K and T_{C2}=247.1 K in Im-ClO$_4$.

Table 1. Values of the critical exponent α and the interaction parameter JA for the temperature intervals indicated.

	Phase	**-JA**	**α**	**Temp. interval (K)**
T_{C1} = 245.8 K	Ferroelectric ($T<T_C$)	31317 ± 1437	**0.33 ± 0.03**	245.2-245.7
	Paraelectric ($T>T_C$)	49926 ± 21234	**0.26 ± 0.09**	245.9-246.5
T_{C2} = 247.1 K	Ferroelectric ($T<T_C$)	40403 ± 3598	**0.30 ± 0.03**	246.6-246.9
	Paraelectric ($T>T_C$)	6411 ± 1915	**0.66 ± 0.13**	247.3-247.9

Finally, the Gibbs free energy ΔG of Im-ClO$_4$ was calculated according to the thermodynamic equation, that reads

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

Regarding the prediction of the enthalpy $\mathit{\Delta H}$ (Eq. 7) and the entropy $\mathit{\Delta S}$ (Eq. 8) for ImClO$_4$, our extracted values of the critical exponent α and interaction parameters from the obtained [11] specific heat data of this crystal (Table 1) were used. Our results were given in Figs. 2 and 3, as a function of temperature for the enthalpy and entropy, respectively. Our predictions for $\mathit{\Delta H}$ (Fig. 2) and $\mathit{\Delta S}$ (Fig. 3) can be compared with the measured values when they are available in the literature. Finally, the Gibbs free energy of Im-ClO$_4$ has been calculated through Eq. (9) using our predicted values of the enthalpy (Eq. 7) and the entropy (Eq. 8), as given in Fig. 4.

3. Discussion

Phenomenological studies relating the critical behavior of some thermodynamic quantities with the theoretical models can construct a bridge for the nature of the phase transition mechanism. Being a simplified lattice model of ferromagnetism, the Ising model has been applied to various systems such as the human brain, alloys, and ferroelectric materials.
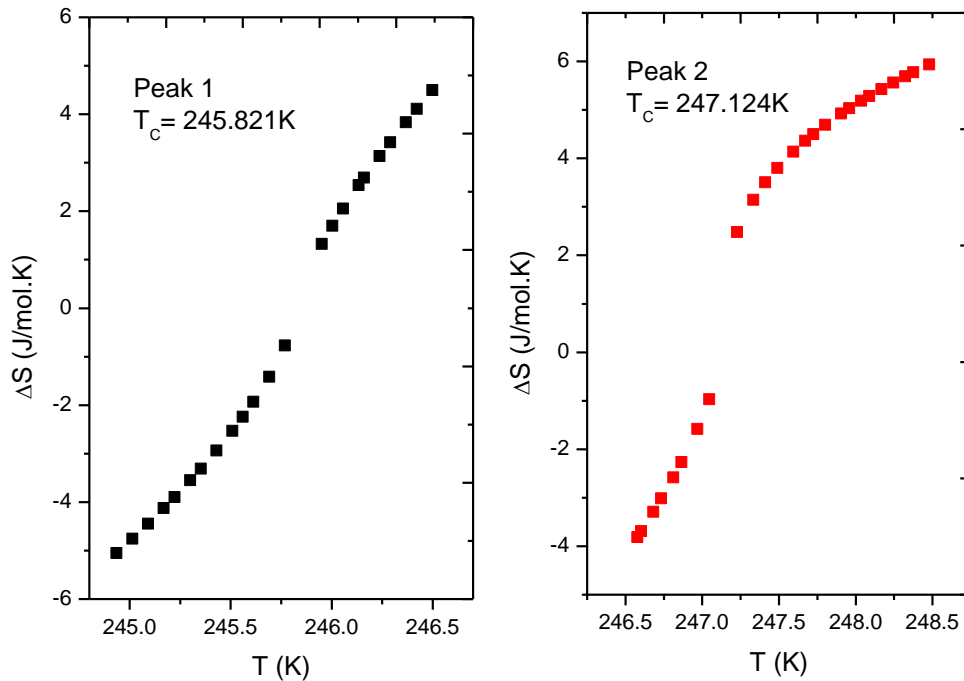
Figure 3. The entropy difference ΔS as a function of temperature according to Eq. (8), close to the phase transition temperatures of T_{C1}= 245.8 K and T_{C2}=247.1 K in Im-ClO$_4$.

Figure 4. The Gibbs free energy difference ΔG as a function of temperature according to Eq. (9) close to the phase transition temperatures of T_{C1}= 245.8 K and T_{C2}=247.1 K in Im-ClO$_4$.
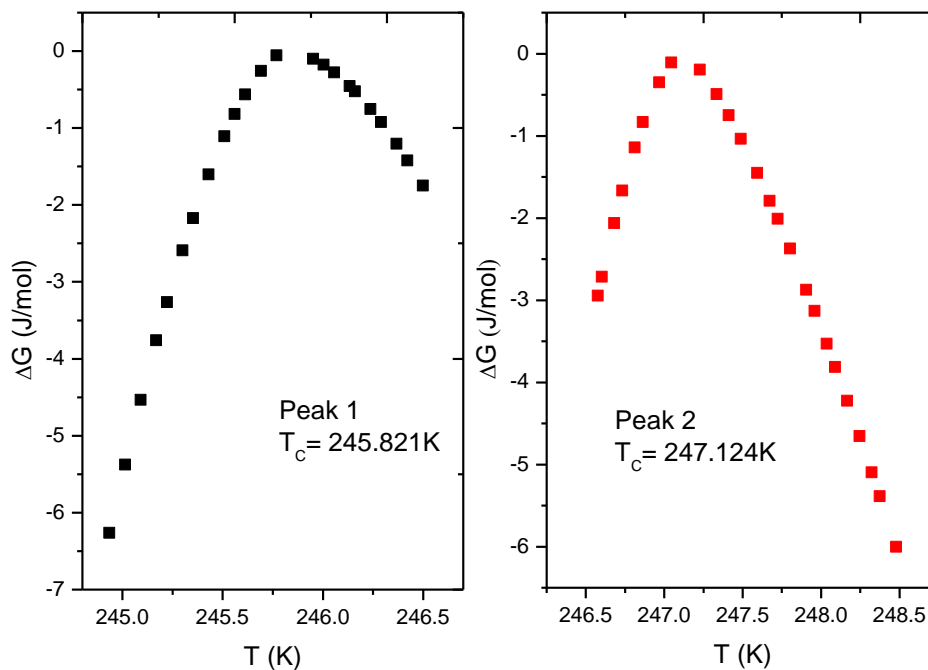
This study contributes to the analysis of the anomalous behavior of the specific heat of a molecular ferroelectric, Im-ClO$_4$, close to the lowest solid-solid phase transition temperature of 247 K from its observed [11] data via the compressible Ising model. The spin interaction and the lattice contributions are the main building blocks of

the observed specific heat data. The former one is responsible for the singular (abnormal) part and is more dominant around the phase transition temperature. The latter is essentially the non-singular (background) part and can be calculated from the theoretical models such as the Einstein and/or Debye models, as stated previously [19]. The spin interaction contribution to the specific heat in the Im-ClO4 crystal is the main subject of this work.

Regarding the analysis of the specific heat of Im-ClO$_4$ crystal, two peaks have been recorded [11] during the specific heat measurement close to the lowest solid-solid phase transition, namely, at 245.8 and 247.1 K, respectively. These two peaks have been considered as the phase transition temperatures, separately. Then, the critical behavior of the observed specific heat data [11] was analyzed according to Eq. (6) close to the transition temperatures of $T_{C1} = 245.8$ K and $T_{C2} = 247.1$ K, as given in Fig. 1. Table 1 gives our extracted values of the critical exponent α and the interaction parameters JA for the temperature intervals indicated. While the values of 0.33 ($T < T_{C1}$), 0.26 ($T > T_{C1}$) and 0.30 ($T < T_{C2}$), can be compared with that predicted from the 2d Potts model (α = 0.30), the value of 0.66 ($T > T_{C2}$) is much greater than the predicted value. So, it is reasonable to argue that the Im-ClO$_4$ undergoes a second-order phase transition at $T_{C1} = 245.8$ K, while it exhibits a first order phase transition at $T_{C2} = 247.1$ K.

4. Conclusion

The phase transition mechanism in Im-ClO$_4$ was investigated by analyzing the specific heat of this crystal close to the phase transition temperature T_C. Our results from the analysis of the specific heat indicate a second order phase transition at $T_{C1} = 245.8$ K and a first order transition at $T_{C2} = 247.1$ K. In addition, some thermodynamic quantities, namely the enthalpy, the entropy, and the Gibbs free energy of this crystal were predicted as a function of temperature in the vicinity of the phase transition temperatures indicated above.

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Declaration of Competing Interest

The author declares that there are no competing financial interests or personal relationships that influence the work in this paper.

Authorship Contribution Statement

Nazan Kara: Reviewing and editing, Methodology, Visualization.

Ali Kiracı: Writing-Original draft preparation, Software, Visualization.

Hamit Yurtseven: Writing-Original draft preparation, Software.

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